1.0 INTRODUCTION

Coal liquefaction will be an important source of transportation fuels in the future, and can be accomplished by both the direct route (hydrogenation of coal in a donor solvent) or by an indirect route (gasification of coal followed by the Fischer-Tropsch reaction).

The product selectivity of the Fischer-Tropsch reaction has been the focus of extensive research for many years, yet still remains a prime target for technical innovation. Fischer-Trospch technology, as it is currently practiced commercially for liquid fuels production, provides a broad range of hydrocarbon products which require costly downstream refining.

Selectivity can be influenced by variations in the catalyst composition and process conditions. Yet, in spite of the extensive effort devoted to this problem, a suitable catalyst has not previously been developed for producing a narrow range hydrocarbon product such as gasoline or diesel fuel without the coproduction of lighter and heavier undesirable products.

The Fischer-Tropsch reaction is also exothermic, and improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Slurry phase reactor operation improves heat transfer and temperature control, and results in greater selectivity to liquid products, usually through lower methane production. However, considerable differences have been reported in the space-time yield, catalyst life and ease of operation of slurry phase reactors.

In addition to improved product selectivity, slurry phase operation offers the advantage of ease of scale-up and the ability to directly utilize the carbon monoxide-rich synthesis gas produced by coal gasifiers. The full potential of the slurry phase Fischer-Tropsch process has not yet been realized, and its further development is an important part in our country's program to establish viable technology for converting coal to hydrocarbon fuels.

Therefore, Air Products (APCI), under contract to the DOE, has undertaken a program in catalyst and reactor development for a slurry phase Fischer-Tropsch process. This contract spans 36 months and is divided into four major tasks. This report described the work accomplished during the fifth quarter.

2.0 OBJECTIVE

The overall objective of this program is to evaluate the catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single stage, liquid phase process.

Task 1 - To establish a detailed Project Work Plan.

Task 2 - To evaluate and test catalysts for their potential to convert synthesis gas to gasoline, diesel fuel, or a mixture of transportation fuels suitable for domestic markets, and to quantify catalyst activity, selectivity, stability and aging with a target process concept involving a single stage, liquid phase reactor system.

Task 3 - To evaluate through the use of cold-flow reactor simulators the flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas. This includes (1) defining heat, mass and momentum transfer parameters which effect the design of slurry reactors, (2) establish operating limits for slurry reactors with respect to system physical parameters, (3) developing or confirming correlations for predicting the flow characteristics and heat/mass transfer of slurry reactors, and (4) defining the necessary requirements for the design of larger scale reactors.

Task 4 - To develop a preliminary design for a pilot plant slurry phase Fischer-Tropsch reactor.

3.0 SUMMARY AND CONCLUSIONS

3.1 Task 1 - Project Work Plan

This task was completed in the first quarter.

3.2 Task 2 - Slurry Catalyst Development

3.2.1 Sub-Task 2a - Background Studies

A computerized survey of available literature and patents dealing with the conventional and slurry phase Fischer-Tropsch processes and the hydrodynamics of three phase slurry reactors was continued.

3.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

Shakedown tests were made on the 1000 mL slurry reactor, and instrumentation of the second 300 mL reactor was continued.

The product analytical method was modified to analyze, for C_{7-9}, the C_{6+} peak produced in the analysis of the gas phase sample from the C_5/C_6 splitting column.

3.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

(a) Catalyst Preparation and (b) Gas Phase Screening Tests

These sections contain potentially patentable material and have therefore been issued in a supplementary report marked "Not For Publication".

(c) Slurry Reactor Tests

Two tests were carried out in the 300 mL slurry reactor.

The "baseline" catalyst test, incorporating the slurry reactor mass transfer test, used a 19.3 wt% slurry of a reduced commercial sintered Fe_2O_3 ammonia synthesis catalyst promoted with 2-3% Al_2O_3, 0.5-0.8% K_2O, and 0.7-1.2% CaO. The catalyst was prereduced with H_2 in a tubular reactor before slurrying in deoxygenated oil. Using 2:1 H_2/CO syngas at 450 psig and stirring rates of 800, 1200 and 1600 min^{-1}, and space velocities of 150 and 250 h^{-1}, the reactor temperature was increased in 20°C stages from 220 to 300°C.

The hydrocarbon product distributions were uniformly approximated by straight Schulz-Flory plots, as expected for this catalyst. Total syngas conversions ranged from 20 to 58%, with usage ratios less than the 2:1 inlet ratio because of the water gas shift. The run data is currently being analyzed in terms of backmixed gas and liquid, and plug flow gas and backmixed liquid models, and this analysis will be presented in the next quarterly report. At a constant space velocity and 280°C, little effect on conversion was observed of increasing the stirring rate from 800 through 1200 to 1600 rpm. At 300°C, the conversions may have been reduced by an increase in the viscosity of the slurry due to the formation of low melting waxes in the slurry oil.

3.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not For Publication".

3.3 Task 3 - Slurry Reactor Design Studies

Measurements of gas hold-up and solids dispersion were completed for the 90-160 μm and 10 and 20 wt% 45-53 μm iron oxide/isoparaffin systems in the 5" column.

For part of the 90-160 μm iron oxide runs, the distributor type unintentionally changed, since it was found that a 3/4" hole had been formed in the distributor plate by impingement of the iron oxide slurry. However, the effect of this change on gas hold-up appeared to be minor. An increase in gas hold-up with positive slurry flow was observed with the iron oxide slurries, contrary to the silica slurry results, but in general, the gas hold-up results lie between the Akita and Yoshida[1] and Pilhofer and Bach[3] correlations.

Uniform solids concentration profiles were observed for the 45-53 μm oxide slurries at zero and positive liquid flow. With the 90-106 μm slurry, non-uniform profiles were found at zero liquid flow, becoming more uniform at positive liquid flow, which may be due to the large hole distributor plate.

A slurry viscosity apparatus was designed and constructed in which the slurry is suspended by gas agitation for viscosity measurement with a spindle viscometer. The actual measurement is therefore a three phase viscosity, from which the two phase slurry viscosity can be calculated.

The 12" column Experimental Work Plan was approved by the DOE Program Manager, and is included as an Appendix to this report. In addition to the independent variables studied in the 5" column program, different heat transfer internals and distributor hole sizes will be studied. The slurry heat transfer coefficient is an additional dependent variable.

4.0 ACKNOWLEDGEMENTS

The contributions to this program by T. G. Dunlap, J. M. LaBar, M. L. Morris, L. E. Schaffer and E. G. Valagene are gratefully acknowledged.

5.0 RESULTS AND DISCUSSION

5.1 Task 1 - Project Work Plan

This task was completed in the first quarter.

5.2 Task 2 - Slurry Catalyst Development

5.2.1 Sub-Task 2a - Background Studies

Background studies, including a computerized search of current literature and patents, were continued this quarter.

5.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

Shakedown tests were made on the 1000 mL slurry reactor after initial problems due to leaks in valves and gauges, particularly in the differential pressure gauge used to monitor the slurry level. The instrumentation of the second 300 mL reactor continued with completion scheduled for next month.

The initial baseline catalyst slurry test showed that the C_{6+} backflush peak produced in the analysis of the gaseous product from the C_5/C_6 splitting column contained a significant amount of C_{7-9}, which produced some discrepancies in the mass balance and product distributions around the C_{6-7} area. The analytical scheme was therefore modified to use the Carle H 111 g.c. to analyze the gas phase samples for C_{6-9} simultaneously with the standard product analysis. The C_{6-9} analysis results were then incorporated into the overall product distribution computation program. This analytical modification was used in the second slurry run, and was successful in removing product distribution discrepancies at C_{6-7} and gave improved mass balances.

5.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Tests

(a) Catalyst Preparation and (b) Gas Phase Screening Tests

These sections contain potentially patentable material and have therefore been issued in a supplementary report marked "Not For Publication".

(c) Slurry Reactor Tests

(i) Test No. 5871-38-B1 - Baseline Catalyst - Slurry Reactor #1

A baseline catalyst test, incorporating the slurry reactor mass transfer test, was carried out in the 300 mL slurry reactor #1. The catalyst used was a commercial sintered Fe_2O_3 promoted with 2-3% Al_2O_3, 0.5-0.8% K_2O and 0.7-1.2% CaO, ground to less than 325 mesh.

The catalyst was first reduced with H_2 in a gas/solid tubular reactor, and then slurried in deoxygenated Edwards #16 oil under N_2 and transferred to the slurry reactor under N_2. In this way, the reactor was loaded with 173 ml of 19.3 wt% slurry.

The slurry was then contacted with a constant 2:1 H_2/CO ratio syngas, at a constant pressure of around 450 psig, using stirring rates of 800, 1200 and 1600 min^{-1} and space velocities of 150 and 250 h^{-1} (based on slurry volume), while increasing the reactor temperature in stages through 221, 241, 260, 280 and 300°C. Table 1 summarizes the parameter range of the samples, and lists the usage ratio of the syngas and the CO, H_2 and CO + H_2 conversions that were obtained.

Although initial difficulties were experienced with the refrigeration unit serving the C_5/C_6 splitting column, and the premature failure of a bursting disc and a power outage, both of which shut the reactor down, the test ran successfully for a total run time of 709.2 hours over a 31 day period. Approximately 18 hours were allowed for the reactor/condenser/sampling system to come to equilibrium after making any process condition change, before carrying out material balances over a 6 hour period on CO and H_2.

An initial problem was experienced in the C_{6+} peak of the gas phase product sample, which was found to contain significant amounts of C_{7-9}. The analytical method was altered to accommodate this, and material balances to within 2-3% were then obtained for both H_2 and CO.

Representative samples are shown in Table 2-15 and Figures 1-14. The hydrocarbon product distributions obtained were uniformly approximated by straight line Schulz-Flory distributions, as expected for this type of catalyst, with average values of α of 0.71-0.72.

The premature failure of a bursting disc at 134 hours caused the loss of 2 ml of slurry into the reactor vent tube, and also allowed partial contact of the hot slurry with air. This resulted in a decrease in the catalytic activity of the slurry, as can be seen by comparing the conversion levels of samples 24 and 28 in Table 1.

Over a further period of 330 hours of operation, the differential pressure gauge recorded a small accumulation of higher boiling products in the reactor, which would contribute to the residual discrepancies in the material balances. At 460 hours, slugs of liquid developed in the oil reflux condenser preventing further accurate monitoring of the slurry liquid level. In the latter stages of the run at 300°C, an attempt to transfer oil from the reactor caused a rapid blockage of the 5 µm stainless steel sinter attached internally to the slurry outlet lines. When the reactor was dismantled, a net loss of liquid from the reactor of ~20 mls was found, but this was accounted for by semi-solid hydrocarbon deposits found at some points in the reflux condenser and gas outlet lines. It is thought that this was due to liquid entrainment in the reflux condenser caused by too high a superficial gas velocity, and improvements will be made to enlarge the bore of the condenser tube to prevent this in future runs.

The residual slurry in the reactor had, over the period of the run, equilibrated with the higher boiling Fischer-Tropsch products, as evidenced by the fact that the slurry had become semi-solid at room temperature. Analyses of the slurry oil and catalyst from the reactor are currently being carried out.

The water gas shift reaction was in evidence at all the reaction temperatures studied as can be seen from the high CO_2/H_2O ratios in the product gas. Its effect increased with temperature, leading to a decrease in the usage ratio of the synthesis gas to 0.9 at 300°C.

The data from this run is currently being analyzed in terms of two models: totally backmixed gas and liquid, and plugflow gas and backmixed liquid, to distinguish mass transfer and chemical rate resistances. The situation is complicated by the effects of the water gas shift reaction on the available hydrogen concentration, and by the gas contraction in the slurry due to reaction. The analysis will be presented in the next quarterly report. At constant temperature and space velocity, stirrer speed had little effect on overall conversion, e.g. samples 79, 81 and 88 in Table 1, where the stirring rate was increased from 810 through 1200 to 1600 rpm at 280°C and GHSV = 250 h^{-1} over a 44 hour period, but the overall conversion was constant to within 2.3%. The decrease in conversion with time observed at 300°C may be due to an increase in slurry viscosity at this temperature because of the formation of low melting waxes in the slurry oil.

5.2.4 Sub-Task 2d - Metal Cluster Catalysts Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not For Publication".

5.3 Task 3 - Slurry Reactor Design Studies

5.3.1 5" Cold Flow Simulator

(i) Gas Hold-Up in Isoparaffin

Experimental runs were completed for the 90-106 μm and the 10 and 20 weight percent 45-53 μm iron oxide systems, and additional data points were obtained for the 1-5 μm silica system (Tables 16-18 and Figures 15-16).

The silica data confirms the correlation developed for this system:

$$\varepsilon_g = 78.01\ V_G^{0.652}/\rho_{SL}^{1.32} \qquad (1)$$

The iron oxide data shows somewhat larger scatter. For most of the later 90-106 μm iron oxide experiments, another type distributor was unintentionally run. A 3/4" hole had been formed by iron oxide impingement against the underside of the distributor plate (Figure 17). However, the effect of this different type of distributor on gas hold-up appears to be relatively minor. Comparing the 45-53 μm and 90-106 μm runs, there appears to be little effect of different distributors on gas hold-up. In fact, the narrow range of distributor pressure drop in the 90-106 μm runs may account for the less apparent data scatter in Figure 15 compared to Figure 16.

The presence of positive liquid flow seems to increase gas hold-up for the iron oxide system, contrary to what had been observed in the silica system. This increased gas hold-up may be due to the liquid providing greater pressure drop when it is flowing, and hence smaller bubbles. These smaller bubbles would then have a slower rise velocity and hence a higher gas hold-up. This hypothesis will be corroborated later in Task 3 when liquid will be introduced above the distributor.

Non-uniform profiles complicate the decision of which weight percent to use in characterizing the column average gas hold-up behavior. Several weight fraction values will be tried including 1) the middle of the column, 2) the bottom of the column, and 3) an integrated average assuming no inherent effect of liquid flow on gas hold-up.

(ii) Solid Dispersion Results

While the different distributors seemed to have little effect on gas hold-up, the effect on solid concentration profiles was pronounced. Non-uniform solid concentration profiles were observed in the 90-106 μm, zero liquid flow runs only (Figures 18-21). That they were not observed for the 45-53 μm, zero liquid flow runs indicates the importance of either a) providing gas distribution across the entire reactor bottom, or b) using smaller sized particles to obtain optimum catalyst utilization during low slurry flows. Which of these possibilities is causing the observed behavior will be resolved later in Task 3.

In the 90-106 μm system, positive liquid flow, there appears to be a very slight but consistant increase in concentration at the 15" sample port. While the cause of this is unknown at present, its effect on column characterization should be minimal.

To assure that solids profile weight percents were determined accurately, a double blind test was run to check for systematic error. By this procedure, samples of known liquid and solid weight were prepared, and were then analyzed by a different individual. Where as with the silica, the calculated weight fraction was 3.5% larger than the prepared weight fraction, there was no discernable systematic error with the iron oxide.

5.3.2 12" Cold Flow Simulator

(i) 12" Column Experimental Work Plan

The 12" Column Experimental Work Plan was written and approved by the DOE Program Manager. The major sections of the Work Plan include:

1) Apparatus; diagram and equipment discussion
2) Independent variables
3) Dependent variables

Table 19 is a summary of the proposed independent and dependent variables.

In addition to the independent variables studied in the 5" column work, different heat transfer internals and different distributor hole sizes will also be used. Additional dependent variables to the 5" column will be the measurement of heat transfer coefficients. A complete discussion of the equipment and procedure used to measure heat transfer coefficients is included in the Experimental Work Plan, which is attached as an Appendix.

6.0 EXPERIMENTAL

6.1 Task 1 - Project Work Plan

No experimental work.

6.2 Task 2 - Slurry Catalyst Development

6.2.1 Sub-Task 2a - Background Studies

No experimental work.

6.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

In the shakedown tests of the 1000 mL slurry reactor, leaks were found and rectified in several valves and gauges, particularly the differential pressure gauge used to monitor the slurry level. The instrumentation of the second 300 mL reactor continued with completion scheduled for next month.

The gaseous product analysis system was modified to allow further definition of the components of the C_{6+} backflush peak. To do this, the role of the Carle H-111 gas chromatograph (g.c.) was changed from that of H_2O vapor analysis to C_{6+} analysis. Previous runs showed that the amount of water vapor present in the gaseous product stream is small and can accurately be estimated by assuming that the gas is saturated with water vapor at the cold top temperature of the condenser in the C_5/C_6 product splitting column. The poropak QS column in the H-111 g.c. was therefore replaced with a 1/8" x 6' OV-101 column and the column temperature was changed to 70°C. This modification allowed separation of C_6, C_7, C_8 and C_9 from the lighter components which elute as a single peak near the injection time. The H-111 g.c. sample injection and multiplexer control signals were timed to place the C_6-C_9 peaks within a clear window between 6 minutes and 20 minutes in the hot wire channel output from the Carle 397B g.c.

The data reduction programs were modified to accept the data for C_6-C_9 and utilize them along with the C_{6+} backflush area in the calculation of each component as below:

$$\frac{A_X}{A_H} \times C_{C_{6+}} = C_X$$

Where: A_X = H-111 component response
A_H = Total of C_6-C_9 H-111 response
$C_{C_{6+}}$ = C_{6+} backflush reported concentration
C_X = Corrected component concentration

This data proved valuable in minimizing the slight discontinuity shown in some experimental Schulz-Flory plots around the C_6-C_7 area.

6.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Tests

(a) Preparation of Modified "Conventional" Catalysts and (b) Gas Phase Screening Tests

These sections contain potentially patentable material and have therefore been issued in a supplementary report marked "Not For Publication".

(c) Slurry Reactor Testing

(i) Test No. 5871-38-B1 - Baseline Catalyst - Slurry Reactor #1

The catalyst used was a commercial sintered Fe_2O_3 promoted with 2-3% Al_2O_3, 0.5-0.8% K_2O and 0.7-1.2% CaO, ground to less than 325 mesh.

Prior to use in the slurry phase, the catalyst was first reduced in a gas/solid tubular reactor under hydrogen at a temperature of 450-500°C for 58 hours and at 1 atm and a GHSV ~1000 h^{-1}, followed by a further 6 hours at an increased pressure of 150 psig. After this treatment, the reduced pyrophoric powder was slurried in deoxygenated Edwards #16 oil and transferred to the slurry reactor under a N_2 atmosphere. In this way, the reactor was loaded with 173 mL of 19.3 wt% slurry (31.85 g of reduced catalyst in 133.01 g oil). After pressuring with H_2 to 450 psig at a GHSV of 70 h^{-1}, the slurry was heated to an initial temperature of 220°C over a period of 19 hours while stirring at 800 rpm.

The slurry was then contacted with a constant 2:1 H_2/CO ratio syngas, at a constant pressure of 450 psig, using stir rates of 800, 1200 and 1600 min^{-1} and space velocities (based on slurry volume) of 150 and 250 h^{-1}, while increasing the reactor temperature in stages through 221, 241, 260, 280 and 300°C. The results are given in Table 1-15 and Figures 1-14.

6.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not For Publication".

6.3 Task 3 - Slurry Reactor Design Studies

6.3.1 5" Cold Flow Simulator

(i) Equipment Modification

Because the high weight percent slurry precludes the use of a Venturi or other flow measuring device, a bucket placed in line to the system is used to monitor flow rate. The problem of solid accumulation with the 90-106 μm iron oxide in the bucket necessitated the construction of a new bucket of modified design.

Owing to sifting difficulties, a five gallon reservoir tank was substituted for the 100 gallon one to allow experimental runs to continue with a smaller amount of solid. In the five gallon tank, the slurry is suspended by sparging nitrogen through a perforated plate distributor. Meanwhile, several outside sifting contractors have been located and samples sent to them for evaluation to ensure that sufficient material will be available for the later column runs.

(ii) Slurry Viscosity Measurements

A slurry viscosity apparatus was designed and constructed in order to more accurately model the bubble column, particularly gas hold-up. Because prior attempts to measure slurry viscosity were unsuccessful in mechanically suspending the high weight percent slurries, a gas distributor is used in this new apparatus. The measurement is thus of a three phase system viscosity, from which the two phase slurry viscosity will be calculated.

To calculate the slurry viscosity, the assumption is made that

$$\mu_{3\phi} = \varepsilon_g \mu_g + (1-\varepsilon_g)\mu_{SL} \qquad (2)$$

where $\mu_{3\phi}$, μ_g and μ_{SL} are the three phase, gas and slurry viscosities respectively, and ε_g is the gas hold-up. Control tests will be run prior to data acquisition to confirm or deny this assumption.

A design schematic of the apparatus is shown in Figure 22. Nitrogen at known temperature, pressure and flow is distributed to the bottom of the column, which has been fully charged with a known slurry sample. After about 15 minutes, the spindle viscometer is lowered, and viscosity measurements are usually made at several spindle speeds and heights.

7.0 REFERENCES

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